



Advances in Organic Synthesis

Editor:
Atta-ur-Rahman, *FRS*

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Edited by

Atta-ur-Rahman, *FRS*

*Kings College,
University of Cambridge,
Cambridge,
UK*

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PREFACE

The 14th volume of *Advances in Organic Synthesis* presents recent exciting developments in synthetic organic chemistry. The chapters are written by authorities in the field. This volume features contributions focused on “on-water” and “in-water” synthesis strategies for heterocyclic transformations, ionic liquid based polyoxometalates as functionalized organic-inorganic hybrid materials, synthesis and bio-applications of some oxygen and sulphur containing seven membered heterocyclic compounds, applications of nitriles in the synthesis of 5-membered azaheterocycles and the role of carbon-based solid acid catalysts in organic synthesis.

This book should prove to be a valuable resource source for organic chemists, pharmaceutical scientists and postgraduate students seeking updated and critically important information on recent important developments in synthetic organic chemistry. I hope that the readers will find these reviews valuable and thought-provoking so that they may trigger further research in the quest for new developments in the field.

I am thankful to the efficient team of Bentham Science Publishers for the timely efforts made by the editorial personnel, especially Mr. Mahmood Alam (Director Publications), Mr. Obaid Sadiq (in-charge Books Department) and Ms. Asma Ahmed (Manager Publications).

Prof. Atta-ur-Rahman, *FRS*
Kings College
University of Cambridge
Cambridge
UK

List of Contributors

Ajay Sharma	Medicinal and Natural Product Laboratory, Department of Chemistry, Chandigarh University, Gharuan-140413, Mohali, Punjab, India
Ayushi Sethiya	Synthetic Organic Chemistry Laboratory, Department of Chemistry, MLSU, Udaipur, India
Claudia R.B. Gomes	Fundação Oswaldo Cruz, Instituto de Tecnologia em Fármacos, Rua Sizenando Nabuco 100, Rio de Janeiro, RJ, Brasil
Dharambeer S. Malhi	Medicinal and Natural Product Laboratory, Department of Chemistry, Chandigarh University, Gharuan-140413, Mohali, Punjab, India
Harvinder S. Sohal	Medicinal and Natural Product Laboratory, Department of Chemistry, Chandigarh University, Gharuan-140413, Mohali, Punjab, India
Jay Soni	Synthetic Organic Chemistry Laboratory, Department of Chemistry, MLSU, Udaipur, India
Marcus V.N. de Souza	Fundação Oswaldo Cruz, Instituto de Tecnologia em Fármacos, Rua Sizenando Nabuco 100, Rio de Janeiro, RJ, Brasil
Manvinder Kaur	Medicinal and Natural Product Laboratory, Department of Chemistry, Chandigarh University, Gharuan-140413, Mohali, Punjab, India
Nusrat Sahiba	Synthetic Organic Chemistry Laboratory, Department of Chemistry, MLSU, Udaipur, India, 313001
Pankaj Teli	Synthetic Organic Chemistry Laboratory, Department of Chemistry, MLSU, Udaipur, India, 313001
Ruli Borah	Department of Chemical Sciences, Tezpur University, Napaam-784028, Tezpur, Assam, India
Shikha Agarwal	Synthetic Organic Chemistry Laboratory, Department of Chemistry, MLSU, Udaipur, India, 313001
Sonali Garg	Medicinal and Natural Product Laboratory, Department of Chemistry, Chandigarh University, Gharuan-140413, Mohali, Punjab, India
Susmita Saikia	Department of Chemical Sciences, Tezpur University, Napaam-784028, Tezpur, Assam, India
Victor Facchinetti	Fundação Oswaldo Cruz, Instituto de Tecnologia em Fármacos, Rua Sizenando Nabuco 100, Rio de Janeiro, RJ, Brasil

CHAPTER 1

“On Water” and “In Water” Strategies for Heterocyclic Transformations

Nusrat Sahiba¹, Pankaj Teli¹ and Shikha Agarwal^{1,*}

¹ Synthetic Organic Chemistry Laboratory, Department of Chemistry, MLSU, Udaipur, India, 313001

Abstract: Water is the most precious and essential element for the sustainability of life. It has emerged as a versatile solvent for various chemical transformations in recent times. It is a naturally abundant, cheap, non-toxic, inexhaustible, and non-flammable green solvent that possesses several unique physiochemical properties like hydrogen bonding, stays in a liquid state at a high range of temperatures, high dielectric constant, large surface tension, and heat capacity. These features make water a powerful domain for the eco-friendly and green synthesis of heterocycles *via* both in-water and on-water methods. Diversified heterocyclic moieties are formed in an aqueous phase through various organic reactions like multi-component reactions (MCRs), pericyclic, Wittig, Michael, Mannich, Aldol, Suzuki, Sonogashira, hydroformylation, and other organo-catalyzed reactions with high atom economy, stereo-selectivity, and sustainability. This article gives a systematic, comprehensive, and authoritative study of a range of reactions in which water is used as a solvent for the synthesis of heterocycles. This article endows an impetus to explore the synthetic and mechanistic aspects of “on” and “in” water reactions and gives insights into the divergence between on-water and in-water synthesis.

Keywords: Atom-economy, Catalysis, Green solvent, Heterocycles, Multi-component reaction, Organic synthesis, Organo catalyzed reactions, Water.

INTRODUCTION

Heterocycles are highly ubiquitous molecules in organic chemistry, having gigantic applications in diverse areas like pharmaceutical, industrial, agriculture, and many more [1 - 3]. They are widely found in nature in nucleic acids, alkaloids, vitamins, proteins, enzymes and, plant pigments, *etc.* In the past century, several imperative heterocyclic core structures have been designed and synthesized by researchers having broad synthetic utility and medicinal values

* Corresponding author Shikha Agarwal: Synthetic Organic Chemistry Laboratory, Department of Chemistry, MLSU, Udaipur, India, 313001; E-mail: shikhaagarwal@mlsu.ac.in

[4, 5]. These heterocyclic transformations occurred in different environmental conditions using various reagents, catalysts, additives, and solvents *via* different strategies like conventional heating, stirring, MW irradiation, mechanochemical grinding, sonication, and so on [6 - 8]. Previously, most of the methods included harsh and toxic reaction conditions like high temperature, harmful reagents and solvents, toxic-gases, waste-generation, and tedious-workup, *etc.* However, in the past decades, after the introduction of 12 principles of green chemistry [9, 10], researchers tend towards the new and innovative eco-benign technologies *via* reducing the negative impact of organic synthesis on mother-nature. The use of safe and less-toxic solvents is one of the important aspects of green chemistry. In organic chemistry, solvents play an important role either as reaction-media or by participating themselves in the reaction [11, 12]. Various chemical-industries employ most of their energy on solvent-treatment [13], which enforces our attention towards replacing the toxic and hazardous solvents with safe and eco-benign ones. Most of the organic solvents are toxic, carcinogenic, mutagenic, corrosive, have low-flash point, deplete the ozone layer and cause many more adverse effects on human beings and the environment [14, 15]. From this point of view, scientists move towards green solvents like water, supercritical carbon dioxide, ionic-liquids, and bio-solvents [16 - 18]. Water is a natural solvent with unique chemistry and is involved in various biological processes and synthesizes diversified stereoselective bio-molecules in the living-organisms. Water is a non-flammable, non-toxic, non-pollutant, and inexpensive solvent with special characteristics like viscosity, polarity, H-bonding ability, immiscibility, high heat-capacity that improves the yield and selectivity of products [19]. The variation in the amount of salt, surfactant, and pH value in water is possible and this special feature enhances the probability of various reactions in an aqueous medium. In 1980, Rideout and Breselow disclosed water-mediated Diels-Alder reactions [20]. After a long time, in 2005, Sharpless and co-workers evolved aqueous-mediated cycloaddition reactions in the heterogeneous mixture and they term these reactions as “on-water” reactions [21]. Afterward, a number of studies performed oxidation, pericyclic, Wittig, Michael, Mannich, Aldol, Suzuki, Sonogashira, hydroformylation reactions [22 - 33], using water as a solvent for sustainable and green synthesis (Fig. 1). Recently, many researchers worked on water-mediated organic synthesis to develop diversified bio-active molecules by following the principle of green chemistry [34 - 45].

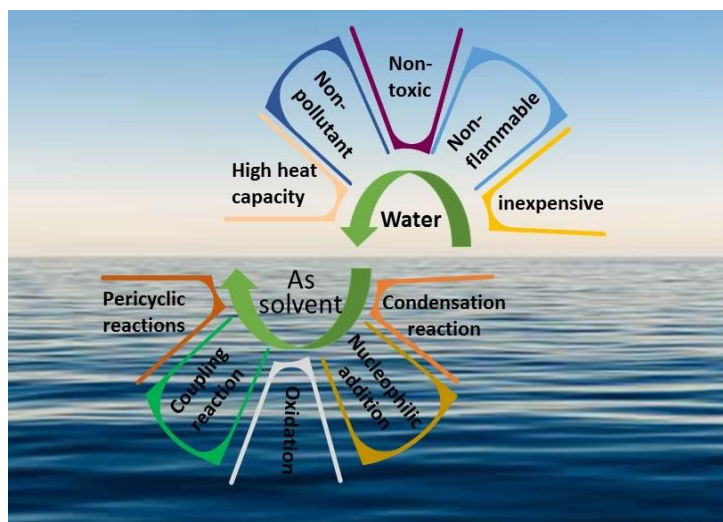


Fig. (1). Green properties of water and its applications in organic synthesis as a solvent.

Previously, various review articles have been published on this topic, which worked as introductory for readers on water-based synthesis [46 - 50]. This chapter focuses on recent aqueous-mediated heterocyclic transformations in different environmental conditions using either catalyst-free synthesis or different catalysts like acid, base, metal, nanocatalyst, and so forth, covering the literature from the year 2010 to 2020.

ON-WATER AND IN-WATER SYNTHESIS

Various water-based heterocyclic transformations are carried out in different physical and environmental conditions of water named as on-water, in-water, hot-compressed water, near-critical water, subcritical and supercritical water, *etc.* [51 - 54]. Among the aforementioned types, “on-water” and “in-water” are the most popular and common terms used in research articles. Sharpless and co-workers introduced the term “on water” and is used when reactants are insoluble in water-phase and make a bi-phasic system, oil-water emulsion without using other organic co-solvent. The rate of reaction accelerates in the oil-water emulsion by hydrophobic effect and H-bonding. Another important term “in-water” is used when the reactants are completely soluble in water (Fig. 2) [21]. However, complete differentiation between both types from naked-eyes is a little difficult because various parameters like physical and kinetic factors affect the reaction mechanism. Therefore authors generally use the terms “synthesis in aqueous conditions”, “water-based” and “water-assisted” synthesis.

Ionic Liquid Based Polyoxometalates as Functionalized Organic-Inorganic Hybrid Materials for Catalytic Organic Reactions

Susmita Saikia¹ and Ruli Borah^{1,*}

¹ Department of Chemical Sciences, Tezpur University, Napaam-784028, Tezpur, Assam, India

Abstract: Functionalized organic-inorganic hybrids of ionic liquids (ILs) with Keggin polyoxometalate (POM) anions of heteropolyacids have received considerable attention in the catalytic study as homogeneous/heterogeneous catalysts owing to their combined unique structural flexibility of the POM anions and tunable behavior imparted by the ionic liquids to the organic-inorganic hybrid of POMs (IL-POM). This includes enhancement of thermal and chemical stability, acidity, surface activity, redox properties, *etc.* The attachment of Brønsted acidic sites such as -COOH or -SO₃H on organic cations of the hybrid materials provides a strong acidic character that can make them appropriate for the replacement of non-recyclable liquid Brønsted acid catalysts in organic reactions. Hydrophobicity, reusability, recyclability, and productivity of these materials certainly satisfy the need for advanced organic synthesis. A large number of designable target-oriented hybrids have been studied as recyclable homogeneous/heterogeneous catalytic systems to explore their industrial values for oxidation and acid-catalyzed organic reactions. This chapter gives a brief introduction to the development of acidic ionic liquid-based POMs hybrid material with varied organic cations tethered with Brønsted acidic sites and their beneficial effects in catalytic organic reactions. The content of this report may provide enormous scope for the development of industrial-scale organic processes based on the IL-POMs hybrid catalysts.

Keywords: Brønsted acidic, Functionalized, IL-POMs, Organic-inorganic hybrid, Organic reaction, POMs.

INTRODUCTION

Polyoxometalates (POMs) and Their Structural Significance

“Polyoxometalates” can be defined as discrete anionic metal-oxygen clusters [1] of oxo metal polyhedra of MO_x ($x = 5, 6$) as basic construction unit where M re-

* Corresponding author Ruli Borah: Department of Chemical Sciences, Tezpur University, Napaam-784028, Tezpur, Assam, India; Tel: +918486541136; E-mail: ruli@tezu.ernet.in

presents early transition metals (M) in their high oxidation states (*e.g.*, W, Mo, V, Nb, Ta) and also partly substituted other metals (*e.g.*, Al, Ti, Cr, Mn, Fe, Co, Ni, Zn, Zr, Ru, Pd, Ln, *etc.*) [2 - 4]. Incorporation of the heteroatom in the anionic metal-oxygen clusters of polyoxometalates generates heteropolyacids (HPAs) in association with proton as their cation. The significance of POMs is observed from their diverse structural variation of polyhedral clusters with unique properties in terms of thermal stabilities, Brønsted acidities, nucleophilicity, crystalline nature, excellent redox behavior, and solubility in polar solvents, *etc.* The structural modification of the POMs framework can be possible in the presence of organic moieties. The unification of varied inorganic and organic parts at the molecular level produces a diverse type of organic-inorganic hybrids with provision for variation of the required properties. It thus furnishes new opportunities for designing target-specific hybrid material. The nature of the organic part may be biostructures such as enzymes, proteins, amino acids, or other functionalized organic molecules that undergo immobilization on the inorganic part through physical or chemical interactions to get the organic-inorganic hybrid with advanced properties of both the components. For example, Zara *et al.* introduced functional organic-inorganic hybrid nanoflowers (FNFs) of immobilized enzymes using proteins/enzymes as the organic parts and Cu^{2+} as the inorganic part in a phosphate-buffered saline solution with remarkable activities and stabilities as compared to free and conventionally immobilized enzymes [5]. From then onwards, a number of protein/enzymes containing flower-shaped organic-inorganic hybrid nanostructures have been developed as biomaterials that take advantage of nanomaterials in terms of both functional and structural availability. This offers new routes for improving the biological functions of enzymes and expands their applications in areas such as biosensors, bioanalytical devices, and industrial biocatalysis [6 - 16].

In the case of organic-inorganic hybrids of POMs, a large number of ionic liquids-based materials have been developed to get target specific systems involving incorporation of different organic cations from ionic liquids to the anionic clusters of POMs with added advantages of enhanced hydrophobic nature, rising solubility in nonpolar solvent, higher thermal and chemical stabilities, increasing Brønsted acidic strength, modification of redox properties, *etc.*, [17 - 19]. These ionic liquid-based hybrids of POMs are designable and flexible enough to tune with the diverse physicochemical properties of ionic liquids through variation of organic cations, which deal in multiple ways to introduce different functionality in the POMs hybrid. The limited numbers of inorganic cations, mainly H^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Ag^+ , *etc.*, are less likely to undergo any modification. Polyhedral framework in POMs has the ability of artificial tuning based on their structural variation, which instigates nature like acidity, basicity, redox stability, and chirality. Several classical structural types of POM anions

such as Keggin, Wells–Dawson, Lindqvist, Anderson–Evans, Weakley, Finke, Silverton, Stranberg, *etc.*, can be used for the same [20]. Among them, Keggin-, Dawson- and Lindqvist-type species have earned a special place in POM chemistry as they function as excellent candidates for the multistep elaboration of POM based materials. The Keggin type structures are the most desirable structures in catalysis due to their unique stability and they have been broadly studied for decades (Fig. 1) [21].

The tuned properties of POMs have been extensively explored in various areas (Fig. 2), including catalysis, medicine, materials science, nanotechnology, molecular magnetism and photochemistry, *etc.* [22 - 34].

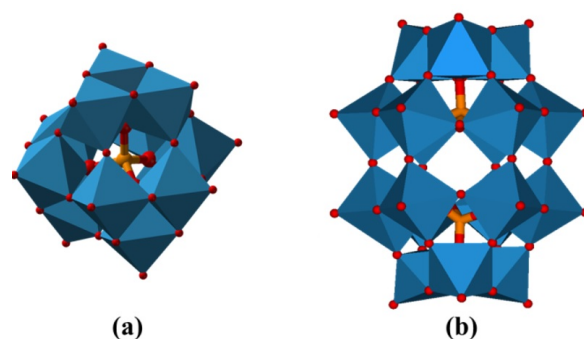


Fig. (1). (a) Keggin structure ($XM_{12}O_{40}^{n-}$) & (b) Dawson structure ($X_2M_{18}O_{62}^{n-}$).

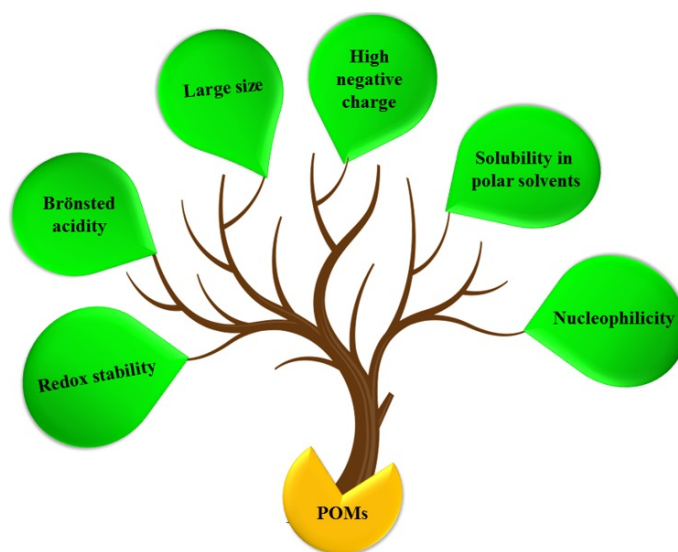


Fig. (2). Properties of POMs.

CHAPTER 3

Recent Advances in the Synthesis and Bio-applications of Some Oxygen and Sulphur Containing Seven Membered Heterocyclic Compounds

Sonali Garg¹, Manvinder Kaur¹, Dharambeer S. Malhi¹, Harvinder S. Sohal^{1,*} and Ajay Sharma¹

¹ Medicinal and Natural Product Laboratory, Department of Chemistry, Chandigarh University, Gharuan-140413, Mohali, Punjab, India

Abstract: Most of the heterocyclic compounds are pharmaceutically active and have numerous applications in various industries. Rigorous effects have been done and still going on in the search for more dynamic and advantageous compounds. Many researchers have focused their work on the synthesis of lower member heterocyclic compounds. However, not many efforts have been made for the higher membered compounds, though having equipotency. The aim of the current study is to collect and document the data available in the seven-membered heterocyclic compounds *i.e.* oxepin and thiepine compounds. The present study includes natural sources, drugs, synthetic methods, reactions, and biological activities of these compounds and their derivatives. Various seven-membered heterocyclic compounds have been synthesized *via* Friedel-craft Cyclization, Ullmann cross-coupling, Sonogashira coupling, and *etc.* However, biological potencies have still not been explored much by the researchers. This encouraged us to write this book chapter, as it has too much scope for future research.

Keywords: Anti-fungal, *Bauhinia purpurea*, *Bauhinia variegata*, Benzothiepine, Benzoxepin, C-O coupling, C-S coupling, Dibenzoxocinone, Dibenzoxepinone, Friedel-craft Cyclization, Intermolecular Cyclization, Intramolecular Cyclization, *Juncus effuses*, Michel Addition, Oxepine, Ptaeroxylin, Pterulinic acid, Sonogashira coupling, Thiepine, Ullmann cross-coupling.

INTRODUCTION TO O & S CONTAINING SEVEN MEMBER HETEROCYCLICS

Heterocyclic compounds are based on a variety of synthetic [1] and natural mole-

* Corresponding author Harvinder S. Sohal: Medicinal and Natural Product Laboratory, Department of Chemistry, Chandigarh University, Gharuan-140413, Mohali, Punjab, India; E-mail: drharvinder.cu@gmail.com

cules [2]. In certain cases, hetero(poly) cyclic rings of different sizes form the backbone of drugs [3], bioactive molecules, and even specialized materials. Heterocycles are of vast significance for industrial, biological, and for the well working of human beings. Heterocycles are there in numerous natural products as well as pharmaceutically active compounds [4 - 8]. During recent years, there has been an intense investigation of different classes of heterocycles. Industrial researchers worldwide have synthesized heterocyclic compounds under ordinary and exceptional conditions, because these reactions are reliably and economically effective. Several different techniques have been developed in the past for the synthesis of different heterocycles, and this advancement is still in ceaseless demand [9 - 11]. The construction of heterocycles is highly considerable in organic synthesis [12]. The chemistry of heterocyclic compounds in organic chemistry continues to be an important field because of their variety of applications. Considering the fact that most of the pharmaceutical and agrochemical items contain at least one heterocyclic ring, we can assuredly see the significance of heterocyclic compounds. Also, a number of natural products depend on heterocyclic units only as a portion of the biologically active compound, for example, vitamins, antibiotics, and hormones [13, 14]. Heterocyclic compounds have become immensely important in human life, especially since these compounds have been successfully tested against several diseases and therefore needed medicinal imports. Heterocyclic compounds are common in nature and necessary to live. They play a key role in every living cell's metabolism. Heterocyclic compounds containing nitrogen, oxygen, and sulfur are essential building blocks used to construct different chemical compounds of immense biological or medical importance [15].

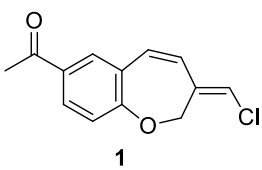
Medium-sized heterocyclic rings are the key in modern organic chemistry because of their ubiquity in Nature [16, 17]. Therefore, the synthesis of medium-sized rings is an important yet challenging goal in modern organic chemistry [18, 19]. An extensive research attempt has focused on the advancement of various methods for preparing a medium-sized rings, including macrocyclization [20], annulations [21], and ring expansion [22]. However, medium-sized heterocyclic rings are measured as complex structures to access because of their adverse transannular interactions to facilitate the synthesis of the desired product and entropic factors that disfavor cyclization. Benzene fused heterocycles become the center of attraction because of its wide scope of pharmacological activities [23]. Few methods exist for their synthesis. Furthermore, many well-designed strategies for the construction of these rings depend upon metal catalysis [24, 25]. Therefore, various novel methods for the synthesis of these heterocyclic rings are highly desirable.

From the literature study of the last 10 years, it was concluded that there is no such report present, which can portray the present situation going on in the synthesis and biological properties of O & S-containing seven-membered heterocycles. Although very few reviews are accounted for to date [26a-e, 27]. So this motivates us to write a report from 2010 to date which can describe the present situation of O & S-containing seven-membered heterocycles. In this review, we have mainly focused our interest on the synthesis and reaction of O & S-containing seven-membered heterocycles.

O-CONTAINING SEVEN-MEMBERED HETEROCYCLES

Oxepin is the seven-membered heterocycles containing Oxygen as a heteroatom. Oxepin and hydrooxepin homologous are core skeletons in many naturally occurring biologically active compounds. These compounds can also be used as an intermediate in the heterocycle synthesis [28] because of which their synthesis gained much attention. The carbon-oxygen bond formation is the simplest method for synthesizing oxygen-containing heterocyclic rings in organic synthesis [29]. Benzoxepines are broadly dispersed in a variety of pharmacologically active compounds and natural products [30], for example, pterulinic acid [30a] (**5**), and ptaeroxylin [30b]. The dibenzo[b,f]oxepins moiety is somewhat rare in nature, and a maximum of them possess exciting medicinal properties [31]. In contrast to any other oxepin derivative, dibenz[b,d]oxepine derivatives synthesis has always been challenging for the researchers. Recently, dibenzo-[b,f]oxepins moiety have been isolated from the natural product by chemists, mainly from plants such as *Juncus effuses*, *Bauhinia variegata*, and *Bauhinia purpurea* [32] (Table 1). Dibenzoxocinone and dibenzoxepinone are the basic moieties that are used in biologically active molecules, for example, Isoxepac (**16**) (for anti-inflammatory) [33], Arugosin F(**19**) (for Antifungal) [34], and Fluradoline (**20**) (for Analgesic drug) [35] (Table 2). Dibenz[b,d]oxepinones derivatives are of great significance.

Table 1. The natural product containing fused oxepin moiety.

S.No.	Name	Structure	Sources	Biological Activity
1.	Pterulone [36]	 <p style="text-align: center;">1</p>	Isolated from mycelium and liquid cultures of wood-decay fungus in the genus <i>Pterula</i> .	Antibacterial, Antifungal properties

Application of Nitriles on the Synthesis of 5-Membered Azaheterocycles: An Update from 2014 to 2020

Victor Facchinetti¹, Claudia R. B. Gomes¹ and Marcus V. N. de Souza^{1,*}

¹ Fundação Oswaldo Cruz, Instituto de Tecnologia em Fármacos, Rua Sizenando Nabuco 100, Rio de Janeiro, RJ, Brasil

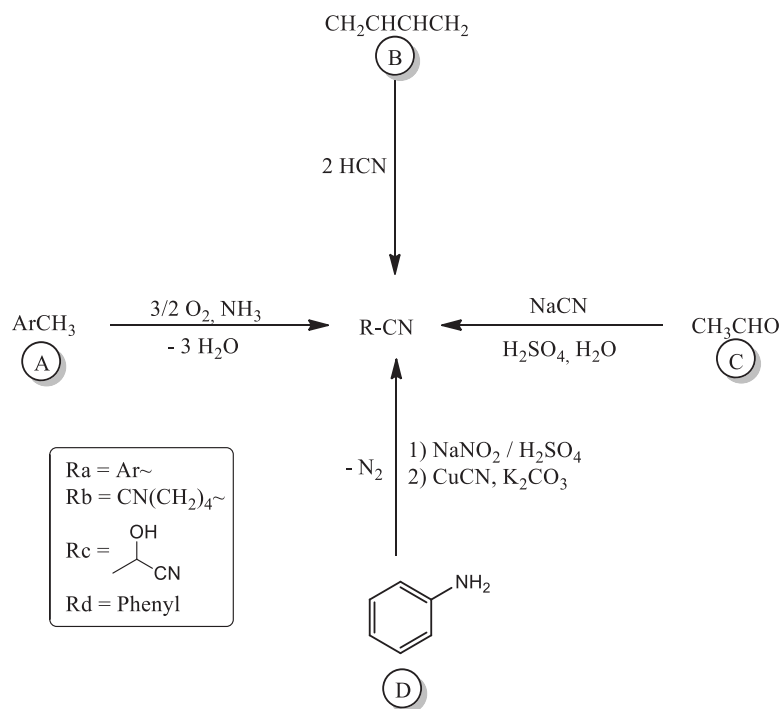
Abstract: Nitriles are organic compounds bearing the $-C\equiv N$ functional group and thus derivatives of hydrocyanic acid. Besides their application in polymers, nitriles are also present in more than 30 pharmaceuticals, including antidepressants, antidiabetics, and anticancer drugs, since they can act as hydrogen acceptors, increase water solubility and shield the drug from oxidative metabolism. Moreover, nitrile derivatives are usually stable and inexpensive and can be converted into many functional groups and heterocycles, and, therefore, are very interesting precursors in the synthesis of robust molecular libraries in medicinal chemistry. It is also important to mention that 5-membered azaheterocycles are of the utmost importance in the medicinal chemistry field, being present in many marketed top-selling drugs. In this context, this chapter will provide an update on the synthesis of prominent 5-membered azaheterocycles from nitriles, focusing on the most interesting reactions and methodologies reported from 2014-2020.

Keywords: Azaheterocycles, Imidazoles, Indoles, Nitriles, Pyrazoles, Pyrroles, Synthesis, Tetrazoles, Triazoles.

INTRODUCTION

Nitriles are organic compounds bearing the $-C\equiv N$ functional group and thus derivatives of the hydrocyanic acid. The prefix Cyano is also widely used in reference to this functional group [1]. In nitriles, both the carbon atom and the nitrogen atom show a sp hybridization, forming a triple bond ($\sigma_{sp-sp} + 2\pi$ bonds) with a bond length around 116pm in acetonitrile. Nitrile derivatives can be synthesized through various pathways such as ammoxidation, hydrocyanation, the formation of cyanohydrins, and the Sandmeyer reaction (Scheme 1) [2 - 4].

* Corresponding author Marcus V. N. de Souza: Fundação Oswaldo Cruz, Instituto de Tecnologia em Fármacos, Rua Sizenando Nabuco 100, Rio de Janeiro, RJ, Brasil; E-mail: mvndesouza@gmail.com



Scheme (1). Some methods for the preparation of nitriles: Ammoxidation (A), hydrocyanation (B), Cyanohydrin formation, (C), and Sandmeyer Reaction (D).

Besides their application in polymers, nitriles are also present in more than 30 pharmaceuticals, including antidepressants, antidiabetics, and anticancer drugs (Fig. 1), since they can act as hydrogen acceptors, increase water solubility and shield the drug from oxidative metabolism [5 - 8].

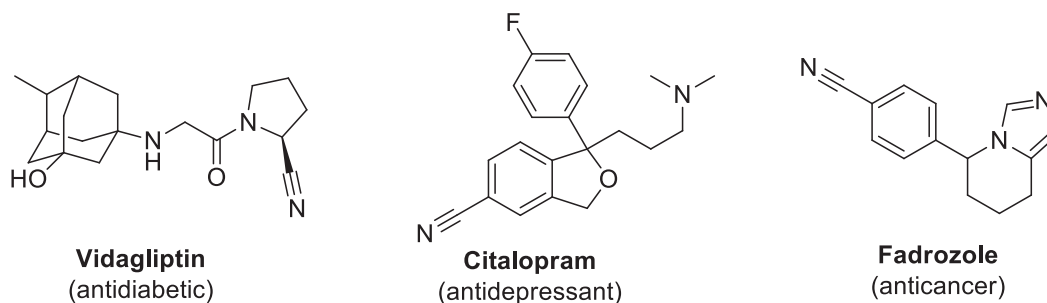
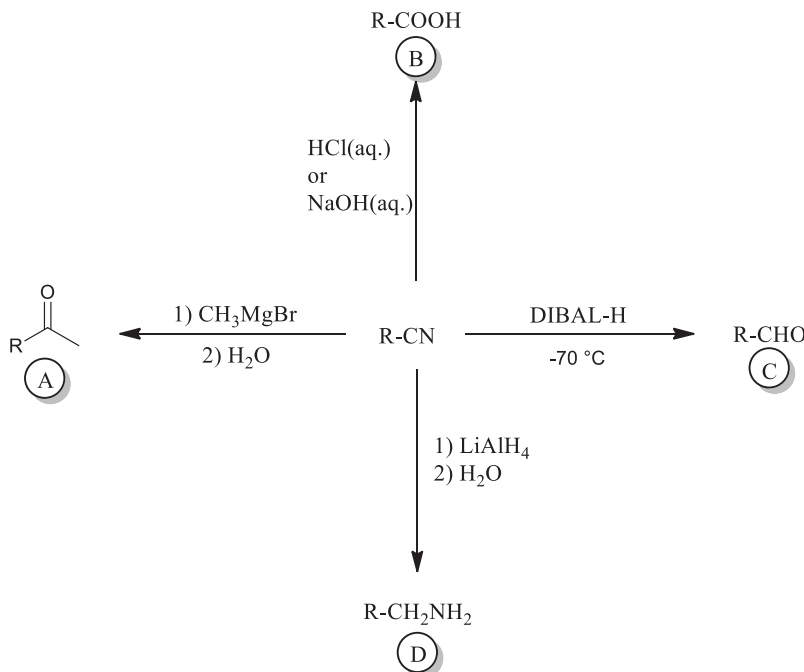


Fig. (1). Example of Nitrile-containing compounds in clinical use.

Moreover, the majority of nitriles are relatively stable and inexpensive compounds that support a high variation of substituents and can be converted into many functional groups (Scheme 2) and heterocycles by various processes. Therefore, nitriles are interesting reagents in the synthesis of robust and diverse molecular libraries that may be used in high throughput screening assays on the search for novel drug candidates [9, 10].



Scheme (2). Example of the conversion of nitriles into some common functional groups: ketone (A), carboxylic acid (B), aldehyde (C), and amine (D).

Five membered-ring azaheterocycles have been extensively explored in medicinal chemistry and are present in many marketed drugs. Some of them, such as pyrrole, indole, triazole, and imidazole are found in top-selling drugs [11, 12] and many more are found in bioactive molecules [13, 14].

Therefore, considering the importance of the nitrile functional group as a precursor to many azaheterocycles, in this work we will review the new synthetic methodologies, reported from 2014 to 2020, for the synthesis of some prominent 5-membered azaheterocycles *via* nitrile intermediates.

PYRROLE AND INDOLE

Pyrroles and its derivatives are important 5-membered heterocycles, which are

CHAPTER 5

The Role of Carbon-based Solid Acid Catalysts in Organic Synthesis

Jay Soni¹, Ayushi Sethiya¹ and Shikha Agarwal^{1,*}

¹ Synthetic Organic Chemistry Laboratory, Department of Chemistry, MLSU, Udaipur, India, 313001

Abstract: In synthetic organic chemistry, heterogeneous catalysis has opened a new era for progressive green and eco-benign synthesis. Fundamentally, it is interminably interesting and perennially novel. Carbon materials are widely used for renewable energy and environmental studies. Significant advancements have been achieved in modern organic chemistry by replacing conventional acid catalysts with pollution-free, recyclable, and eco-benign solid acid catalysts to reduce toxicity and increase efficiency. Solid acid catalysts play a profound role in organic synthesis as they are heterogeneous, recyclable, ease of workup, corrosion-free, immiscible in routine organic solvents, easy recovery from the products, selective synthesis, *etc.* Furthermore, carbon-based solid acid catalysts have attracted scientists because of its simple preparation method, increased acidity, selectivity, high stability, easy separation of products, no corrosion of equipment, easy recovery and recyclability, *etc.* They exhibit remarkable catalytic activity for various acid-catalyzed reactions, such as biofuel production, hydration, hydrolysis, and esterification of higher fatty acids. This article profoundly discusses the synthesis, properties, and applications of carbon-based solid acid catalysts in organic synthesis.

Keywords: Biginelli reactions, Bio-diesel, Carbon-based solid catalyst, Catalysis, Condensation reactions, Esterification, Green synthesis, Heterocycles, Organic reactions, Synthetic organic chemistry.

INTRODUCTION

Currently, scientists are paying significant attention to design eco-friendly pathways for organic transformations. There has been a spike in the interest of researchers for more environmentally acceptable processes in the chemical industries. This tendency is known as “Green Chemistry” or Sustainable Technology [1, 2]. The basic concept of Green Chemistry is the use of chemical

* Corresponding author Shikha Agarwal: Department of Chemistry, Synthetic Organic Chemistry Laboratory, MLSU, Udaipur, India 313001; E-mail: shikhaagarwal@mlsu.ac.in

skills and knowledge to reduce or eliminate the use or production of toxic substances during the planning, manufacturing, and application of chemicals to minimize threats to the health of operators and the environment [2]. In brief, the principles of Green Chemistry are based on the minimization or non-use of toxic solvents in chemical processes and analyses and the non-generation of waste. One of the best ways of implementing the principles is to use recoverable and reusable catalysts. The catalysts play an imperative role in the reduction of pollution in our environment. It is one of the most elementary pillars of “Green Chemistry”. With the use of catalysts, the reaction becomes more effective, selective and productive, thereby eliminating huge amounts of toxic waste and by-products and also saves resources [3]. They are usually applied for the synthesis of chemical products of industrial and laboratory importance [4]. Thus, catalysts act as a master key in reducing both the investment and operation cost of a chemical process. Acid catalysts are the most important area of catalysts that are studied and developed in recent decades. A variety of industrial reactions are catalyzed by mineral acids or organic acids. Various reactions, such as Friedel–Crafts alkylation and acylation, sulfonylation, aromatic halogenation, nitration, isomerization, and oligomerization occur in the presence of the acid catalysts. The acid catalysts can be categorized into homogenous and heterogeneous acid catalysts according to their states in the reaction. Several mineral acids, such as H_2SO_4 , HCl , HF , H_3PO_4 , etc. are used on a large scale as liquid homogenous acid catalysts, which give the desired products at low temperatures because they mostly involve the reactions in their original molecular state. However, there are few disadvantages of using liquid acid catalysts, e.g., production of a huge amount of waste liquors, tedious separation and filtration of liquid catalysts, the uneasiness of successive reaction operations, etc. These reagents are perilous in handling, detriment the plant through their corrosiveness, and involve process complexities by employing quenching and separation stages. Therefore, the use of mineral acids is undesirable due to the following issues [4]:

- The amount of waste generation is larger than the amount of product formed.
- The waste disposal cost increases the cost of the operation.
- It causes environmental pollution.
- Leads to a separation problem.

In continuation to resolve the problems brought by liquid acid catalysts into the reaction, a survey of environmental-benign and simple recyclable heterogeneous solid acid catalysts becomes meaningful. The great potential of solid acid catalysts has been experienced in synthesizing organic compounds [5 - 8]. Solid acid catalysts are used at a large scale for the acid-promoted processes in organic synthesis [9, 10]. Moreover, they are heterogenized on different solid supports to

reduce the toxicity or increase efficiency [11 - 13]. They are grouped into various parts, such as silica-based solid acid [14, 15], zeolite-based solid acid [16], polymer-based solid acid [17, 18], and carbon-based solid acid [19 - 21], and so on, as shown in Fig. (1).



Fig. (1). Different types of solid acid catalysts.

CARBON-BASED SOLID ACID CATALYST

From the last few years, carbon materials have become a prominent topic in the research area as they are used to catalyze several reactions [22]; in lieu of this, carbon-based solid acid catalysts are developing rapidly. They have served as precious materials for industrial process and organic reactions because of its several advantages that are appended below and also shown in Fig. (2).



Fig. (2). Various catalytic properties of a carbon-based solid acid catalyst.

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PROF. DR. ATTA-UR-RAHMAN, FRS

Prof. Atta-ur-Rahman, Ph.D. in Organic Chemistry from Cambridge University (1968) has 1,232 international publications (45 international patents and 341 books). He received the following awards: Fellow Royal Society (FRS) London (2006), UNESCO Science Prize (1999), Honorary Life Fellow Kings College, Cambridge University (2007), Academician (Foreign Member) Chinese Academy of Sciences (2015), Highest Civil Award for Foreigners of China (Friendship Award, 2014), High Civil Award Austria ("Grosse Goldene Ehrenzeischen am Bande") (2007), Foreign Fellow Chinese Chemical Society (2013), Sc.D. Cambridge University (UK) (1987), TWAS (Italy) Prize (2009). He was the President of Network of Academies of Sciences of Islamic Countries (NASIC), Vice President TWAS (Italy), Foreign Fellow Korean Academy of Science & Technology, President Pakistan Academy of Sciences (2003-2006) and (2011 – 2014). He was the Federal Minister for Science and Technology of Pakistan (2000 – 2002), Federal Minister of Education (2002) and Chairman Higher Education Commission/Federal Minister (2002-2008), Coordinator General of COMSTECH (OIC Ministerial Committee) (1996-2012), and the Editor-in-Chief of Current Medicinal Chemistry.